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ELECTROLYTIC REGENERATION OF ACID CUPRIC CHLORIDE
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by

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ELECTROLYTIC REGENERATION OF ACID CUPRIC CHLORIDE
(Quarterly report #1)

I. SUMMARY OF ACCOMPLISHMENTS

During the quarter we ran tests to determine the effects that key plating parameters have on copper deposit quality. Parameters tested include (a) velocity past the plating cathode, (b) copper concentration in the catholyte from which the copper is plated, (c) plating current density, and (d) catholyte cupric content. The most significant effects were obtained for velocity changes. We also tested porous cell separator materials for hydrophilicity, and evaluated graphite felt activation life from 2 preparation methods.

II. TASK ACTIVITIES AND RESULTS

Task 1. Parametric Studies

A. Plating Parameters

One of the major goals of the first quarter work was to study the effect that changes in some of the key process parameters have on deposit quality and other process measurements.

One parameter, whose importance was seen in a pair of runs just prior to the start of this grant effort, is catholyte velocity past the plating electrode. In those runs, we installed an "eggcrate" gap-filler in the plating cell cathode chamber and got dramatically improved deposits. The eggcrate assembly that we built - shown in figure 1 - fills almost 2/3 of the gap cross-section with pockets of still electrolyte, thereby increasing velocity in the cathode chamber by a nominal factor of 2.5. Using the "eggcrate" gap reducer is an inexpensive and easy way to get higher velocities in the pre-prototype test system's plating cell since it avoids the need to make new thinner chamber frames or fatter center plates, or to have to handle significantly higher flow quantities through the unit.

To study the velocity effect in a more systematic way we made a series of additional runs with and without the "eggcrate" assembly. A first set of 3 runs was done at 6.2 A plating currents. These velocities varied from 0.37 to 0.52 to 1.35 ft/sec. The deposit quality was much better at the high velocity. Grains on the surface were significantly smaller at 1.35 ft/sec than at the lower flow rates indicating that additional hours of plating

would be less likely to grow dendrites there. All deposit coupons were fairly uniform in thickness, indicating uniform current densities.

Another group of runs was made at 7.5 A plating current and flows of 0.54, 0.96 and 1.48 ft/sec. Again the deposit is finer (smaller grains) at the highest velocity and poorest (coarsest grains) at the lowest velocity, although the gradation from best to worst was not as dramatic as at the lower current plating. Again, deposit plates were uniform in thickness and appearance. The velocity variation data clearly show the advantages of higher flow rate. With the higher flow rate it is possible to get decent deposits at higher current densities than would otherwise be possible. This translates to smaller plating areas at a particular copper deposition rate requirement, i.e lbs/hr, and thus fewer (or smaller) cell modules. The reduced plating surface comes at the price of handling more gpm through each plating module. Since the space available to install inlet and outlet lines on modules is little different from pre-prototype to commercial scale unit - set to a great extent by the 3/8" gap needed to accumulate a day's copper deposit with space still left for flow past the cathode afterwards - this probably means pressurized cells and more difficult cell sealing.

A second plating parameter we looked at was the overall concentration of copper in the catholyte. It is known in plating that generally higher concentrations of the species being plated favors production of an improved deposit. We made runs at both 6.2 and 7.5 Amps where we employed concentrations of 21-23, 32-34, and 41-42 g/l of total copper in the catholyte at fixed flow rates. Each set showed the expected improved deposits with increased concentration, however differences in quality (smaller grains at higher [Cu]) were modest. Doubling of concentration (21-23 to 41-42 g/l) had much less effect on deposit quality than doubling flow rate in the tests described above. Increased copper concentration results in lower electrical efficiencies in our process - all other things being equal - since each gallon of etch fed to the catholyte to replenish copper plated has to also provide the replacement copper in the gallon of catholyte that is removed to make room for the incoming etch. That means more total electrolysis is needed at high catholyte copper/high replenishment than at low copper/low replenishment. It doesn't look like the highest copper concentrations pay the increased current cost - not to mention the increased precipitation possibilities - with enough deposit improvement to make them worthwhile.

Much of the work on this project has been done to evaluate the effect of plating current density, with the goal being to get good plating quality at increasingly higher currents. In this report period, we looked at how plating varied over the range of 6.2 A (80 mA/cm^2) to 8.7 A (112 A/cm^2). In the runs made to do this, all other important parameters were held essentially

constant (flow of 0.96 ft/sec, and [Cu] at 21-22 g/l). As expected, deposit quality fell off with increasing current density, though not to a dramatic extent. It appears that the higher flow rate used for these runs was able to mitigate the effects of increased current density to a significant degree. The increase in roughness - larger deposit grain size - with current was significantly less than in earlier studies where increases in current density from 4.2 A (54 mA/cm²) to 6.2 A (80 mA/cm²) were tested at 0.35 to 0.51 ft/sec flow rates. An important parallel here is the increasing voltage drop at the plating cell with increasing plating current. From less than 2 volts at 6.2 A, it rose to about 2.35 volts at 8.7 A. This obviously reflects the higher iR drop and electrode potential, and indicates that 112 mA/cm² operation is near the highest current at which our goal of a 2 volt drop in the commercial unit is attainable.

The last parameter studied in the quarter was catholyte's cupric concentration and whether it too affects deposit quality. Our measure of cupric in the catholyte is the solution ORP. At a fixed catholyte total copper concentration, solution ORP varies directly, but not linearly, with cupric content. We typically operate at a catholyte ORP of 230-250 mV, which corresponds to about 1 g/l Cu²⁺. The lower limit is the point where it typically becomes difficult to maintain knockdown cell current flow without plating on that cell's cathode, while the higher value corresponds to a solution for which the plating cell spends too much cathodic current converting cupric to cuprous ion.

To test the catholyte [Cu²⁺] effect, we made a set of 3 runs at 6.2 A using about 40 g/l total copper in the catholyte. Catholyte ORP levels were 219, 239 and 256 mV; these correspond to about 0.4, 0.85 and 1.5 g/l of cupric respectively. Deposits made in these runs all looked the same with uniform thickness and relatively small grain size. The biggest difference from run to run was deposit weight; as expected, the deposit weight fell as ORP increased. The deposit weight at the highest ORP was 88% of the copper recovered at the lowest ORP. Since there was no significant difference in plate quality, there isn't any major advantage in operating at the ORP extremes.

B. Separator Material Studies

In early work with the pre-prototype system, we learned about the importance of having a hydrophilic separator between the anode and cathode compartments of the cells - particularly for the plating cell. When we used off-the-shelf porous polyethylene, we got dendritic, non-uniform deposits, reflecting poor current distribution (typically high at the bottom of the cell and low near the top). Application of a topical surfactant significantly

enhanced the separator's wettability and promoted uniform current density and good copper deposits with constant cross-sections. However, the treatment was continuously leached out and had to be re-applied periodically. To avoid this, we switched to a separator plate made with porous alumina which our tests showed to be both hydrophilic and unattacked by the electrolyte.

In the commercial scale unit, we will also need a porous hydrophilic material with good chemical resistance and moderate cost. Porous glass has desirable physical properties but is too expensive. Other porous ceramics are available, but etch solution reacts with them. Porous plastic is economical and won't be attacked by the process solutions, but as discussed above, it is not hydrophilic. Discussions with vendors, however, indicated that there might be processing which could solve this problem. Consequently, we sent out samples of porous polyethylene and propylene for plasma and radiation treatments. Plasma treated porous polyethylene samples have been received from Anatech Ltd, so, during the quarter, we designed a test to measure hydrophilicity and used it on these and other porous specimens.

The test consists of dropping water from a buret onto framed specimens (PVC cement painted on the perimeter of pieces to define a test area of 1 to 2.25 in²) that are sitting on a lightly dampened sponge. We use a 5 minute maximum period, or 25 ml maximum volume, and follow the volume of water over time that is passed through into the sponge. Table I shows results for plasma treated and untreated porous polyolefin samples and a piece of the porous alumina now used in the pre-prototype cells. It is apparent that all 3 levels of plasma treatment made the porous polyethylene hydrophilic; the data shows that untreated it allows no water penetration. The larger pores account for the significantly higher water flow through the plastic vs the ceramic.

In the next month, we will retest the plasma treated samples after stirring them with 50-60°C etch solution. When radiation treated samples come in they will also be tested, along with other porous materials we find in the work.

Task 2. Graphite Felt Activation

While there are a number of important discoveries that have enabled development of this regeneration process, almost certainly, none is as important as the use of high surface area electrodes. Graphite felt is what we use (other high area materials could be employed) in the knockdown cell and as the plating cell anode. Previous work with earlier versions of these electrodes indicate that they might have been too short-lived. It is imperative for process acceptance in the real world that the felt maintains performance for "adequate" periods of time.

One measure of felt life is obtained by following the electrochemical behavior of electrolyte adjacent to the felt during process electrolysis. We measure solution potentials at the electrodes versus Ag/AgCl reference electrodes during electrolysis runs; that's one of the standard data items used to determine performance. The change in potentials over time, with the comparisons made at otherwise constant conditions, is an indication of felt changes.

The usefulness of this method is shown in Table IIA. There, we have listed solution potentials at an electrode (at times when essentially equal current and flow existed) vs. charge passed (Ah_{rs}) over the first six months of operation of the pre-prototype scale regenerator. This was done for both the plating cell and the knockdown cell anodes, though the table only shows knockdown cell anode data. The increased potential as total charge passed increased, indicates that the felt deteriorated over time. Similar analysis showed comparable deterioration in the plating cell anode and knockdown cell cathode. Because the knockdown cathode is typically operated at constant potential, the knockdown cell cathode's loss of activity was shown by the need to hold a higher cuprous concentration in the catholyte (higher catholyte ORP) in order to support a particular knockdown cell current.

The first set of felt electrodes used in the pre-prototype system (the electrodes used in the first six months of operation) all appear to have ebbed to a condition of too little activity to handle current densities of 65-75 mA/cm² after about 450 - 650 hrs of operation. All these were made by heating in air, in a furnace, to 450°C.

The current set of pre-prototype felt electrodes were made using steam to activate the felt. These we heated in an atmospheric pressure, steam-flushed chamber to 500°C. As shown for the knockdown anode in Table IIB, the new electrodes have exhibited significantly longer lives than the initial set. The 1327 Ah_{rs} of operation of the knockdown cell operation with the Table IIB anode is more than double the 600-630 Ah_{rs} when the first knockdown cell anode was seen to operate poorly, and the new electrodes are operating at higher current densities - 80-95 mA/cm² - which is a more difficult environment too). Still, recent sensitivity of the new knockdown anode's potential to modest etch ORP increases, indicates that its activity may be falling off. Unexplained too, is the poor activity that this electrode showed over the first 250-300 Ah_{rs} of operation - the other steam-activated felt electrodes in the system now, started up right away with very reasonable potentials.

Because of the relatively long life we are now seeing with the graphite felt electrodes, it will be difficult to determine relationships between activation method and felt activity life at the pre-prototype level. That is due to the limited speed at which experiments can be run in the system. At the larger prototype level however, accumulating 1000 Amp-hrs (per unit of pre-prototype electrode area) will only take about a week, so electrode life trends will be seen much faster. Consequently, that's obviously the place for in-depth evaluation of electrode life vs. activation method. However we will be testing activation techniques or variations in method from time to time in this phase of the work, with initial electrode behavior our preliminary measure of performance.

Table I
Test Results: Porous Separator Materials

	<u>Volume Water to Sample Surface over Time, mls</u>					
Sample No ⁽¹⁾	1	2	3*	4	5*	6*
1 min	2.7	0.35	2.8	0.6	1.1	3.7
2 min	2.8	0.35	4.1	0.75	5.8	10.0
3 min	2.95	0.35	8.6	0.75	20.8	23.0
4 min	3.1	0.35	22.6	0.75	25.0 ⁽³⁾	25.0 ⁽⁴⁾
5 min	3.15	0.35	25.0 ⁽²⁾	0.75	-	-
remainder ⁽⁵⁾	0	0.3	0	0.7	0	0

Notes

(1) Sample ID's

- #1 1/4" 100% alumina porous ceramic plate
- #2 1/4" UHMW porous polyethylene (20 micron pores)
- #3 1/4" plasma treated porous polyethylene (90 micron pores) 150 Watt, 1 torr, 2 min
- #4 1/4" porous polypropylene (120 micron pores)
- #5 1/4" plasma treated porous polyethylene (90 micron pores) 50 Watt, 1 torr, 3 min
- #6 1/4" plasma treated porous polyethylene (90 micron pores) 75 Watt, 1 torr, 3 min

(2) 25 ml passed in 4' 15"

(3) 25 ml passed in 3' 22"

(4) 25 ml passed in 3' 11"

(5) Water removed from surface @ end of test. A value here indicates that sample was hydrophilic

* Sample surface was 2.25 in² (all others 1 in²)

Table II

CHANGES IN KNOCKDOWN CELL ANODE BEHAVIOR⁽¹⁾ OVER TIMEA. Hot air, 450°C Furnace Activated AnodeCharge Flow, Ahrs

31.5	153.3	300.1	344.1	405.2	501.2	540.7	612.5	632.9
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Current, Amps

7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.5	7.0
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Anode Potential, mV

950	710	750	840	870	950	990	1060	1450
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B. 500°C Steam Activated AnodeCharge Flow, Ahrs

16	102	192	258	409	603	859	1040	1147	1225	1327
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Current, Amps

8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.6	8.6	8.6	7.7
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Anode Potential, mV

1330	1370	1400	990	710	780	730	800	760	780	780
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Note

- (1) Following potential at the electrode (vs. Ag/AgCl reference) in pre-prototype unit over time when etch ORP = 495-500 mV, temperature = 50°C., and flow through the anode compartment = 0.9-1 liter/min

Figure 1. "Eggplate" Gap Reducer